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New Results of Studies on Coal Structure by Spectroscopic Methods

Hans Henning OELERT and Ernst A. HEMMER

I. Absorption Spectroscopy in the Ultraviolet, Visible, and Infrared Regions

Review paper presented by E.A. HEMMER at the Annual Meeting of the Austrian Society of Petroleum Sciences and of the German Society of Petroleum Science and Petrochemistry
8 October 1968, Salzburg, Austria

Summary

After a brief review of earlier papers the results obtained by work done in the years 1960-1968 are discussed. In addition, for greater clarity, some findings made for coal extracts and tars are reported. This first part of the paper deals with absorption spectroscopy in the visible, ultraviolet, and infrared ranges.

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Introduction

The first comprehensive reports on the structure of coal that gave due weight to spectroscopic findings, were published around 1960[1,2,3].

X-ray diffraction studies indicated that coal had an amorphous and an oriented fraction, the latter consisting of aromatic rings and accounting for 50-80% of the carbon in units of 13-18 carbon atoms[4]. Although the aromaticities thus calculated were in the same order of magnitude as results obtained with other methods, the interpretation of the findings was variously criticized[5,6]. Other authors used x-ray diffraction analysis for macerals and maceral cokes[7]. X-ray fluorescence can be used to determine many elements, mainly those of the inorganic fraction. The same applies to UV emission spectroscopy and atomic absorption spectroscopy. However, these latter methods do not provide data that can be used to elucidate the organic-chemical structure of coal and are therefore merely mentioned here. Absorption coefficients in the visible region were measured with thin sections or finely ground samples[8] in transmitted light or were calculated from reflection measurements[9]. Although all these various studies determined the same qualitative course, i.e. that with increasing wavelength specific absorptions decrease almost at the same rate, the absorption coefficients differed considerably. Generally, absorption increases with increasing rank. It was concluded from the low extinctions of the UV absorption spectra[10,11] and the non-selectivity of absorption that it was not justified to assume the existence of more highly condensed aromatic structures and that an extensive system of tetrahedrically arranged C—C bridges with quaternary carbon in diamond-like structures might exist. Other authors[12] disagreed, arguing

that high aromaticities could be deduced from comparative measurements of coal constituents. This view was confirmed[13] by the adjustment of spectra for mixtures of condensed aromatic model hydrocarbons to extract spectra. Aromaticities of 0.7 to 0.8 were found. Although the measurements in this spectral region as a whole made it plausible for coals to have mainly aromatic structures, quantitative determination proved impossible at the time. In many cases it is possible to detect specific substances usually generated by pre-separation by means of ultraviolet absorption, fluorescence, or phosphorescence techniques. However, it has hitherto been impossible to derive from such individual data a plausible image of the overall composition of coal extracts or tars.

Infrared spectroscopy was used relatively early to study coal[14]. Investigations in the period of 1950-1960, of which here only the major ones relating to coal[15-19] and macerals[20,21] will be mentioned, essentially aimed at the qualitative analysis of the structural groups of coal. There were indications that usually chelated, phenolic hydroxyl groups were present, also aromatic CH groups, methylene groups, and methyl groups. No olefinic double bonds were detected. Several spectral regions gave indications of extensive substitution in the aromatic rings and of various types of oxygen bonds. In the case of macerals it was found that compared to vitrinites, exinites contained more aliphatic structures, micrinites more large closed aromatic structures. A number of studies examined coal constituents. Their findings indicated that the structures of coals and of the substances obtained from them were in principle the same if certain special tar fractions were ignored. From measurements before and after dehydrogenation experiments it was concluded that the number of

aliphatic fractions had decreased[22], from measurements before and after hydrogenation, that some of the aromatics were not hydrogenated[23]. In the first attempt at obtaining also quantitative data[24] a method was developed to estimate the ratio of aromatic to aliphatic hydrogen. It was based on the extinction quotients of stretching bands of model substances. Subsequent tests aimed at determining the hydroxyl group content; both the integral extinctions in this region[25] and the decrease of OH stretching bands after pyrolysis or acetylation[26] were measured.

Nuclear magnetic resonance spectroscopy - broad-line or high-resolution - was used to determine the various proton groups. Comparative measurements with NMR of aromatic model substances and coals revealed correlations that, in the form of an incremental technique, could be used for group analysis of coals[27,28,29]. Although this method permits calculating the relative ratios of various groups to each other, at first it did not succeed in resolving the determination equations down to detailed group determination. Other authors reported limiting factors[30], having found signal intensity to depend on coal rank. The high-resolution technique can be employed only for soluble substances but then provides much more comprehensive data.

Coal constituents were used to test the technique developed on the basis of infrared spectroscopic measurements[24]; this technique gave more detailed information on the types of hydrogen bonds[31,32]. Under certain conditions this information can be used to calculate aromaticity, degree of substitution of aromatic structures, and theoretical H/C ratio of unsubstituted aromatics,

all as characteristic parameters. It could be hoped that, if procedures and resolution were improved, it would be possible to draw more far-reaching conclusions. Mass spectroscopy essentially is suitable only for analyzing coal constituents of sufficient volatility. Although the attempt was made to introduce coals directly into the spectrometer[33-36], investigations of this type fall more into the area of pyrolysis. Studies on coal constituents provided some information on low-molecular fractions[34,36,37], but were able to contribute in a major way to elucidating the overall structure of coal.

Electron spin resonance as a method of coal analysis was used for the first time in the mid-fifties[38,39,40]. All coals and their petrographic components produce signals that indicate the presence of one unpaired electron in every 1 to $5 \cdot 10^3$ carbon atoms. The g value was always found to be very close to 2.0023. The dependence of spin concentration on temperature and coal rank was investigated and conclusions were drawn therefrom on the transformation of aromatic structures[41].

It was the aim of these introductory remarks to present in outline the status of knowledge in 1960. Not all the papers published have been quoted. Overall it can be said that spectroscopic techniques were not used before 1945 and that until 1960 they provided essentially qualitative data and some semi-quantitative information. The work to be discussed below achieved sophistication of qualitative data after 1960, but mainly succeeded in developing methods of quantitative analysis. On account of the techniques used and the nature of the substances in question, the information is largely statistical.

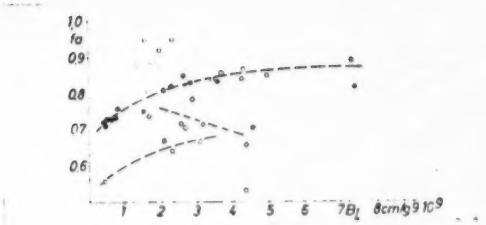
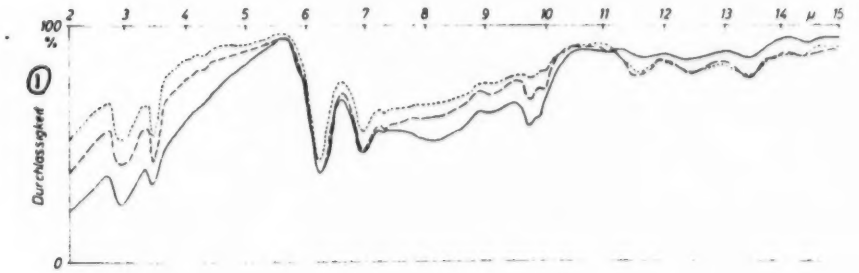


Figure 1. Aromaticities as a function of integral absorption coefficients in the ultraviolet region

- o coals
- • thermally pretreated coals
- ▫ hydrogenated coals
- ϕ chloroform extracts of coals

Translator's note: In the Figures, where applicable, please read commas as decimal points.



---- K 23,5 ($741 \cdot 10^{-4}$ g/cm³), — · — · K 28 ($888 \cdot 10^{-4}$ g cm³), —— K 38 ($733 \cdot 10^{-4}$ g cm³)

Figure 2. Infrared spectra of coals

Key: 1 - transmittance

Absorption spectroscopy in the ultraviolet and visible regions

Studies on low-temperature tars produced at 450°C, on chloroform extracts[42] from shock-heated coals, and on vitrinites[43,44] confirmed the high aromaticities found earlier by other authors[12]. Spectrometry of bituminous coals[45] indicated that, in contrast to anthracites, they contained smaller aromatic structures of different types; this agrees with findings obtained with other methods[46]. Also, it was pointed out[47] that even structures other than aromatic hydrocarbons could contribute to absorption in this range. All authors agree that on account of the variety of absorbing groups in coals and coal constituents, the spectra cannot show any specific bands and no definite qualitative data can be expected.

In studies of our own we tried to determine the quantitative relationships between various coals and to see how our results compared to findings made with other methods[48]. Since essentially we aimed merely at comparisons, we used the KBr pellet technique, despite its limiting factors pointed out by OTVOS et al.[49], for which it has been demonstrated that even in this region Lambert-Beer's law applies[50]. Figure 1 is a plot of the aromaticities of various substances measured by infrared spectroscopy against the integral absorption coefficients B_I determined for the ultraviolet range. For coals containing more than 28% volatiles, B_I rises only little with increasing aromaticities, but it increases rapidly for higher-rank coals. The gap thus indicated is connected to the "coalification step". Other findings[46] allow us to assume that essentially the differences in B_I values are due to the different characteristics of the aromatic structures in different coal ranks both with regard to degree of condensation and to molecular size.

At pretreatment temperatures up to 450°C the values measured for the residues resemble those of the original coals. This indicates that the chemical changes determined by measuring absorption in the ultraviolet range are similar in pyrolysis and natural coalification. At temperatures above 450°C great changes in aromatic structure[51] result in reduced absorption, but with a direct ratio between B_I and aromaticity seemingly persisting even then. By contrast, no satisfactory explanation has yet been found for the fact that hydrogenated coals have comparable B_I values at distinctly lower aromaticities. From the generally different behaviour of extracts it can be assumed that smaller molecules with aromatic structures are extracted first, their absorption coefficients at constant aromaticity being higher than those of the non-extracted polymeric substances in the coal.

Measuring the integral absorption coefficients in the visible region (B_{II}) has shown that there absorption depends much less on coal rank and that thermal pretreatment initially results in rising B_{II} values with a point of inversion at approx. 430°C. These findings overall give the impression that absorption in the visible region is determined primarily by the type and size of the polymeric structures in the coal. Various authors[11,40,41,52] have also discussed the possibility of the free radical concentration affecting coal colour. Comparing radical concentrations with B_{II} reveals a direct relation between them via the carbon content.

Another review of studies using ultraviolet and visible spectroscopy has been published by FRIEDEL et al.[53].

Absorption spectroscopy in the infrared region

Studies that should be mentioned first are work aimed more at qualitative comparisons. It was concluded from the similarity between the spectra of artificial carbonification products from carbohydrates[54] and of various natural coals and coal precursors that the conditions under which these products and coals are formed may be similar and that certain pyrolytic temperatures can be linked to certain ranks. This interpretation agrees with other findings[48,51]. A correlation was established between measurements of quinoline-soluble and quinoline-insoluble fractions of coal tar pitches and the technological behaviour of these substances when heated[55]. Other authors compared infrared spectroscopic with differential thermal analysis data[56].

We shall deal in somewhat greater detail with earlier attempts at quantitative analysis. Measurements of isolated pure substances from coal were used to develop an incremental technique[57] by which aromatic CH group and methyl group concentrations could be determined directly. Figure 2 shows an example of quantitatively evaluable coal spectra. The concentrations of acetylizable hydroxyl groups in coals[57] and lignites[58], too, can be determined infrared spectroscopically. British authors[59] reported another method of determining methyl groups in soluble coal constituents by means of added indicator substances. Techniques were developed[50,60] also to differentiate the various substitutions in aromatic rings. Taking into account elemental composition, the concentrations of most structural groups of coal can be calculated from such measurements[61]. If the results of broad-line NMR[62-66] are included, the data become

even more informative[61]. Recently, primarily studies carried out in Australia[67] showed that not only incremental techniques but also relative techniques are being further verified and developed.

Group analyses of this type can be used to determine the distribution of different types of hydrogen or carbon bonds. However, the results obtained by various authors with different methods are not always comparable. Figure 3 shows aliphatic hydrogen concentrations, obtained with different methods, relative to coal carbon contents. Although the overall trend is the same for all infrared or nuclear magnetic resonance data, there are differences in the absolute values, particularly between lower-rank coals. Figure 4[69] gives the structural group distributions measured infrared spectroscopically for a number of Ruhr coals. In many cases, especially in higher-rank coals, the data on aromatic CH groups compare well with data in the literature that have been suitably converted[70-74]; in other cases, particularly in lower-rank coals, there is less agreement[62,66,75,76,77]. The results for methyl groups agree well with recent literature data[73,78,79], while other values determined mainly chemically[59] are lower. One paper[80] expresses doubts as to the possibility of evaluating absorption bands quantitatively. However, the values in Figure 4 prove that at least the relative accuracy of this method is sufficiently high. As regards the other groups represented in Figure 4, the hydroxyl group concentrations agree very well with most of the data from the literature, and the other data cannot be compared because there are no pertinent data in the literature. These studies show coals to be organic material which essentially has to consist of different highly substituted aromatic structures. Analysis of macerals[68] has shown that

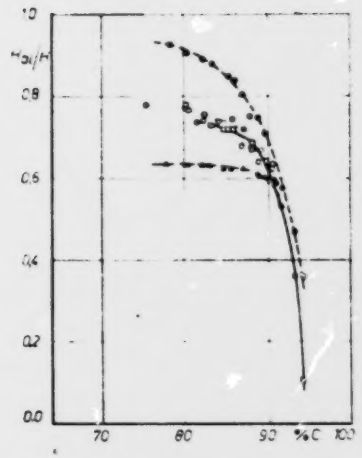


Figure 3. Relative aliphatic hydrogen concentrations as a function of coal carbon content
- ● W.R. LADNER et al.[62]
- □ J.K. BROWN et al.[68]
- ▲ H. TSCHAMLER et al.[63]
- o values of present work

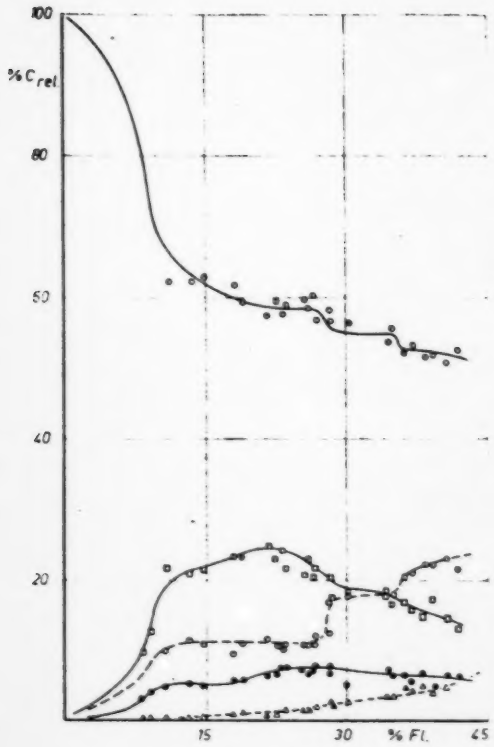


Figure 4. Relative carbon concentrations of various structural groups as a function of the volatile contents in coals. Sequence from the bottom up: C—OH, CH_3, CH_2, CH_{ar}, C_{ar}

%. Fl. = % volatiles

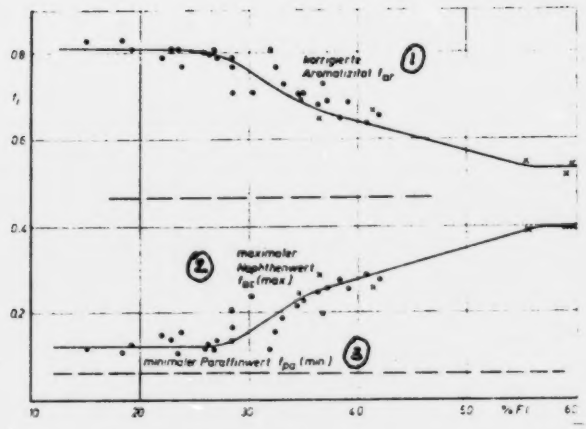


Figure 5. Corrected carbon distribution as a function of volatile content

- ● coals
- o vitrinites
- x exinites

Key: 1 - corrected aromaticity
2 - maximum naphthene value
3 - minimum paraffin value
% Fl. = % volatiles

vitrinites have slightly lower aliphatic group concentrations than exinites which contain distinctly fewer hydroxyl groups. In micrinites the aromatic structures generally seem to occur in more continuous formations. However, such investigations of these types of macerals do not show any great statistical differences with regard to structure. The maceral aromaticities calculated from these measurements agree approximately with the values reported in the literature[21,65,81]. Even more recent qualitative infrared spectroscopy of macerals has not materially increased our knowledge of maceral composition[82]. A study dealing specifically with resinites is worth mentioning[83].

Taking into consideration nuclear magnetic resonance data, basic types of carbon bonds can be calculated for coals and macerals that correspond to the data usually given in mineral oil analysis. Figure 5 shows the course of these parameters across a wide range of coalification. The paraffinic bond fraction derived from the methyl group concentration has been assumed as constant at 6.5%. If we assume this, the decrease in volatiles content can be interpreted as a gradual transition from aliphatic to aromatic structures and supports the view that a considerable portion of alicyclic rings are present in hydroaromatic form that can be dehydrogenated. Moreover, this representation does not point to any basic differences for macerals. From a different angle[68] it becomes clear that the relationship between hydroaromatic and aromatic structures is very pronounced in exinites. The ratio of alicyclic to paraffinic structures will doubtless still require correction. LAHIRI et al.[71] estimate the average paraffin value to be 12%. From this assumption and from the fact that by extraction or pyrolysis of medium-rank coals the order of magnitude of the long hydrocarbon chain fraction is found to be 2%, it can be concluded that in the main coal fraction the methylene and methyl group concentrations shown in Figure 4 come closer together, and

that a not inconsiderable part of the methyl groups is linked directly to aromatic rings. Some naphthene values determined chemically[84,85] are slightly lower than shown in Figure 5. Aromaticity was regarded as significant for analyzing coal structure. Comparisons between the values in Figure 5 and data calculated with other methods[86,87] show good to moderate agreement[68], while earlier literature data[4,29,87] are usually higher[57].

Infrared spectroscopic studies on substitution in aromatic structures of coals[68] have shown that approx. 30% of aromatic hydrogen occurs in arrangements where no, two, or four hydrogen atoms adjoin each other. In the case of macerals it was found that in vitrinites and micrinites the density of substitution is slightly greater than in exinites. Generally, in coals and macerals the density of substitution increases with rank. In coal extracts it decreases with decreasing extraction yields[50]; this agrees with the idea that coal consists essentially of polymeric substances. The semicokes formed during pyrolysis have considerably higher substitution densities[50]; this can be interpreted as the beginning of cross-linking.

If absorptions in the 1640-1540 cm^{-1} range are properly evaluated, infrared spectroscopy can contribute also to the quantitative estimation of carbonyl concentrations. The results of such spectroscopy show that in dependence on rank, 20-80% of coal oxygen may occur in carbonyl groups of presumably predominantly quinoid character. The data obtained by BLOM[88] are similar, but some other authors have found considerably lower concentrations[89,90]. Most recently, various authors[91,92] have attempted to interpret this absorption range from a theoretical viewpoint. While some authors feel[91] that no carbonyl

groups bonded by hydrogen bridges occur, others think that semiquinone structures exist[92]. Recently, the interference in this range by water bands has again been investigated[93].

The group analysis techniques that have been developed can be used also to evaluate chemical changes in structure during hydrogenation[50] and above all during pyrolysis[51,94]. By contrast, a combined method of group analysis, to be discussed later, provides more reliable data for soluble substances such as extracts and tars. Finally we should also mention that it was attempted to use the ATR (attenuated total reflectance) technique in infrared spectroscopy[95] and that non-dispersive infrared analyzers have been successfully employed to analyze the gases generated during pyrolysis[96,97]. FRIEDEL et al.[53] have given an excellent review especially of earlier publications.

Part II of this paper will report on mass spectroscopy and on nuclear magnetic and electron spin resonance spectroscopy.

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